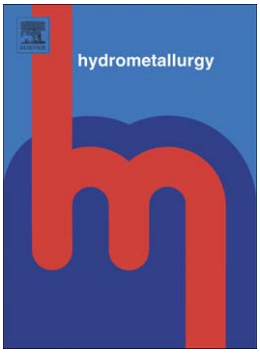

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Decomposition of Bayer process organics: phenolates, polyalcohols, and additional carboxylates

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Abstract

The degradation of nineteen low-molecular-weight phenolates, polyalcohols and selected aliphatic and aromatic carboxylates of relevance to the Bayer process has been studied in 6 mol kg^{-1} NaOH(aq) at 90 °C for up to 36 d, and (for some species) at 180 °C for up to 12 d, using HPLC and ^{13}C-NMR spectroscopy. Aliphatic polyalcohols degraded readily at 90 °C to lactate, oxalate, acetate, and formate. As observed previously, aliphatic carboxylates with hydroxyl groups also degraded readily at 90 °C but there is evidence that the position of the hydroxyl group may be important. The observed degradation products for most, but not all, of these species can be explained in terms of well-known organic reaction mechanisms. Phenolate adn 5-hydroxyisophthalate were stable at 180 °C but other phenolic species degraded partially at 90 °C. However, the reaction products could not be identified and no trends in reactivity were discernible. Consistent with previous studies both aliphatic and aromatic carboxylates without hydroxyl groups were generally stable in NaOH(aq) even at 180 °C.

Keywords: Bayer process; organic compounds; degradation; sodium hydroxide solution, aromatics, aliphatics

1. Introduction

It is widely recognised in the alumina-refining industry that the presence of even relatively small amounts of organic matter in bauxite ores can result in quite high levels of organic species accumulating in Bayer process solutions. Australian bauxites, for example, which typically have total organic carbon (TOC) levels of 0.05-0.5 wt.-% (Whelan et al., 2003) can produce TOC concentrations as high as 40 g/L in Bayer plant liquors (Grocott and Rosenberg, 1988). The organic matter in bauxite ores occurs mainly in the form of high-molecular-weight biopolymers such as humic substances, cellulose, and lignin. The extraction and degradation of this material during the high temperature caustic digestion step in the Bayer process produces a plethora of low-molecular-weight (LMW) organic species (Power and Loh, 2010). These are mainly aliphatic and aromatic carboxylates (Lever, 1978; Guthrie et al., 1984; Whelan et al., 2003), but there are also sugars, polyalcohols, and saturated hydrocarbons (Ellis et al., 2002). Some of these degradation products are gibbsite precipitation poisons (Grocott and Rosenberg, 1988; Power and Tichbon, 1990), some have other detrimental effects on plant efficiency or product quality (Atkins and Grocott, 1988), and still others produce potentially hazardous volatiles such as H_2 (Brown, 1989; Arnswald et al., 1991), CH_4, acetaldehyde, and methylethylketone (Coffey and Ioppolo-Armanios, 2004). The effects of these degradation products are often exacerbated by their accumulation due to the routine recycling of process

liquors (Grocott, 1988; Atkins and Grocott, 1988).

While some qualitative information is available regarding the identity of the organic species present in Bayer liquors (BLs), it is only recently that studies on the reactivity and possible degradation mechanisms of specific substances have appeared in the open literature (Tardio et al., 2004a; Loh et al., 2008a,b; Machold et al., 2009). An ionic reaction mechanism (Loh et al., 2008a; 2010) that involves base-catalysed oxidation by water qualitatively accounts for the formation of a number of liquor-stable components such as acetate and oxalate, as well as H_2(g). The applicability of this mechanism to the degradation of a number of known gibbsite yield inhibitors was demonstrated by Loh et al. (2008a; 2010). A further study of a wide range of LMW carboxylates (Machold et al., 2009) showed that this mechanism accounted well for the degradation of many hydroxylated aliphatic carboxylates which are structurally related to gibbsite yield inhibitors. That investigation also revealed that both aliphatic and aromatic carboxylates with hydroxyl substituents generally degraded much more readily in hot concentrated NaOH(aq) than species lacking such substituents.

The present paper reports the behaviour in hot concentrated caustic solution of representative polyalcohols and phenolates as well as some additional carboxylates. Nineteen organic species were selected for study on the basis of their known or potential relevance to Bayer liquors, as shown in Table 1.

2. Experimental

2.1 Overall procedure

All substrates were of analytical grade, purchased from Sigma-Aldrich (USA), Acros (USA), Univar (Australia), or TCI (Japan), and were used as received. Their degradation behaviour was examined in 6 *m* (mol kg^{-1}) NaOH(aq) solution. Oxygen was rigorously excluded throughout, as described previously (Machold et al., 2009), because it can have a significant effect on the rates and mechanisms of organic degradations in concentrated alkaline solutions (Loh et al., 2008a,b). The aluminium species present in plant Bayer liquors were not included in the test solutions as experiments in the presence of gibbsite showed no differences in degradation products observed and no catalytic effect of the alumina species.

Reactions at 90 ºC were conducted for up to 36 d using the apparatus and procedures detailed previously (Machold et al., 2009). Samples were removed from the reaction vessels after 12, 24, and 36 d then analysed by NMR spectroscopy and HPLC. Reactions at 180 ºC were performed in a 2 L Monel autoclave (Parr, USA) containing approximately 1 kg of reaction mixture. Unless otherwise specified, samples were taken for analysis after 12 d. The temperature of the autoclave was controlled to ± 2.0 ºC using a Parr temperature controller and thermocouple. All solutions were vacuum-filtered through a PTFE membrane (0.45 μm pore diameter, Pall, USA) immediately prior to transfer to the autoclave. The autoclave and its contents were then purged with N_2 prior to heating. Compounds that degraded at 90 ºC were presumed to react similarly at higher temperatures and were therefore not tested at 180 ºC. No significant differences in reaction products or rates were detected between duplicate runs on the same species.

2.2 HPLC analysis

All solvents for chromatography were of HPLC grade (Lab-Scan, Thailand) and were filtered (0.2 μm nylon membrane, Alltech, Australia) immediately prior to use. The preparation of samples, buffers and standard solutions, as well as the HPLC analyses were the same as desribed previously (Machold et al., 2009). In brief, filtered samples (syringe filter with 0.45 μm PTFE membrane, Pall, USA) were separated using a thermostatted (25.0 ± 0.1 °C) Prevail Organic Acid column (5 μm x 4.6 mm x 150 mm, Grace Discovery Sciences, USA) at a flow-rate of 1.0 mL min^{-1}. Aliphatic compounds were detected by their absorbance at 215 nm using a mobile phase of 25 m*M* KH_2PO_4(aq) buffered to pH 2.10 with H_3PO_4. Propanoic acid and aromatic compounds were detected at 215 and 254 nm, respectively, using a mobile phase of 2:3 (v/v) acetonitrile and 25 mM KH_2PO_4(aq) solution buffered to pH 2.10 with H_3PO_4.

2.3 NMR analysis

Structures and ^{13}C-NMR chemical shifts for each organic species are provided in Table 2. This table serves as a useful reference for the discussion of the observed degradation products in section 3 below. Solutions of standard samples (0.1 *m* in 6 *m* NaOD/D_2O) were spiked with a small amount of methanol-d_4 as an internal chemical shift reference (δ_H = 3.34 ppm; δ_C = 49.50 ppm) and gravity filtered into a 5 mm o.d. glass NMR tube. The deuterated solvent was used to facilitate measurement of ^{1}H-NMR spectra; however, such spectra proved to be less useful than the ^{13}C data for the detection of reaction products and hence have not been included here. For the analyses, 1.0 g of the reaction mixture of the organic substance in 6 *m* NaOH(aq) was

mixed with 0.5 g of D_2O (99.75 % isotopic purity) and a small amount of methanol-d_4, and gravity filtered into an NMR tube.

Spectra were obtained using either a Bruker Avance DPX 300 (^{1}H frequency 300 MHz; ^{13}C frequency 75 MHz) or a Varian 400/54/ASC (^{1}H frequency 400 MHz; ^{13}C frequency 100 MHz) with standard pulse sequences. The number of scans collected varied but was typically 128 for ^{1}H spectra and 10,000 for ^{13}C spectra. NMR-data were processed using the Bruker XWin-NMR or Varian VnmrJ software packages. Deuterated solvents were purchased from Sigma-Aldrich.

3. Results and Discussion

Where possible, the identities of degradation products were verified by comparison with standards for HPLC retention times (Table 3) and ^{13}C-NMR spectra (Table 2). The observed stabilities of the species studied in 6 *m* NaOH(aq) are summarised in Table 4. For reasons given previously (Machold et al., 2009), only the relative extent of degradation can be stated. Compounds were considered stable if, over the lifetime of the experiment, there was no discernible change to their ^{13}C-NMR spectra, no decrease in their relative HPLC peak area, and no appearance of significant new HPLC peaks.

3.1 Reactions of aliphatic compounds

The most common degradation products observed for aliphatic species were oxalate and acetate (Table 5). All decomposing aliphatic species produced the former but

acetate was observed only from fumarate, citrate, and the polyalcohols D-glucitol and D-mannitol. The polyalcohols also produced formate and lactate. It is noteworthy that at 90 °C none of the reacting aliphatic species was completely consumed, even after 36 d, indicating rather slow degradation in 6 *m* NaOH(aq) at this temperature.

The present results accord with previous observations (Machold et al., 2009; Loh et al., 2008a,b, 2010) that LMW carboxylates with hydroxyl substituents tend to degrade readily in hot concentrated NaOH(aq). Ionic mechanisms based on well-known organic reactions and base catalysed oxidation by water (Loh et al 2008b, 2010) can account for most of the observed degradation products. Consider, for example, the formation of oxalate (the only degradation product observed in solution, Table 5) from glycolate. This reaction almost certainly begins with the deprotonation of the aliphatic hydroxyl group by OH^- (Figure 1). An aldehyde species (glyoxylate, **1**) is then generated when a C2 hydrogen leaves as a hydride ion during the formation of an oxygen-carbon double bond. The eliminated hydride picks up a proton from water, giving H_2 and re-generating OH^-. Subsequent nucleophilic attack by OH^- on the carbonyl carbon of glyoxylate forms an alkoxide species (**2**) that further reacts with water, with the formation of a second H_2 molecule and oxalate, in a manner analogous to the Cannizzaro reaction (Smith and March 2001). It should be noted that, in the Cannizzaro reaction, the eliminated hydride reduces another aldehyde molecule. Here the eliminated hydride reacts with a water molecule in base-catalysed oxidation by water as described by Loh et al (2008b, 2010). The present experimental set up did not permit detection of vapour-phase products but it can be noted that Costine et al. (2010) detected H_2 during the decomposition of the structurally-related tartrate ion in hot NaOH(aq). Parallel work in our laboratories, which will be reported elsewhere,

has confirmed the formation of hydrogen from other hydroxyl-carboxylates such as malate.

The conversion of citrate to oxalate and acetate (as the only products detected in solution) can be accounted for in a similar manner (Figure 2). Again the process can be thought of as being initiated by deprotonation of the aliphatic hydroxyl group. This is followed by a retro-aldol condensation, leading to the formation of enolate (**3**) and ketone (**4**) intermediates. The former can then be converted to acetate by abstraction of a proton from water. Nucleophilic acyl substitution from attack by OH^- on the carbonyl carbon of the ketone intermediate (**4**) and cleavage of the $-CH_2COO^-$ group results in the formation of oxalate and another acetate ion. Similar mechanisms can be written to account for the observed products from the degradation of related compounds (Loh et al., 2008b, 2010; Costine et al., 2010).

The degradation of fumarate is of particular interest because in NaOH(aq) it forms an equilibrium with malate (Erickson and Alberty, 1959; Machold et al., 2009). Malate itself is a known constituent of Bayer process liquors (Guthrie et al., 1984) and has been used as a model for decomposing organics (Machold et al., 2009). Under the present conditions fumarate probably converts to malate by simple hydration. Furthermore, oxalate and acetate are formed with either fumarate (Table 5) or malate (Machold et al., 2009) as the starting species. The formation of oxalate and acetate from malate is readily accounted for by the mechanism presented previously (Machold et al., 2009), shown here for convenience in Figure 3. In contrast, while oxidative cleavage of the C=C double bond of fumarate might occur under the present reaction conditions, it would produce only oxalate. While we did suggest that oxalate

and acetate might be formed directly from fumarate (Machold et al., 2009) it is difficult to envisage a plausible mechanism for such a reaction. It seems more likely, therefore, that these two products are formed from the malate present in the reaction mixture.

At first glance it may appear that benzilate should be classified as an aromatic compound. However, it is the position of the hydroxy and carboxyl groups that is important in the current context. In benzilate both are located on the aliphatic portion of the molecule that links the two phenyl groups. Hence benzilate has been classified as an aliphatic compound, whereas 3-hydroxy benzoate (Table 2) is considered to be an aromatic compound. On the basis of its hydroxyl group, benzilate (Table 2) was expected to degrade at 90 °C but was instead found to be stable. This lack of reactivity is probably because the hydroxyl group is in an α-position relative to the carboxylate group. Such an arrangement precludes the retro-aldol reaction, which is possible for citrate (Figure 2) and malate (Figure 3) where hydroxyl groups are in β-positions relative to carboxylate moieties. The unexpected stability of benzilate suggests that the presence of a hydroxyl group does **not** always confer reactivity and the position of these groups relative to carboxylate groups is a factor. It is noteworthy that glycolate (Figure 1, Table 2) also has the hydroxyl group in an α-position relative to the carboxylate group but it is unstable. The difference in reactivity between benzilate and glycolate may be accounted for on the basis of leaving group ability. The C2 hydrogen atoms of glycolate can be eliminated as hydride ions (Figure 1) but under the same conditions the C2 phenyl groups of benzilate are not eliminated.

In contrast with benzilate, tricarballylate (Table 2) might have been expected, due to

its lack of hydroxyl groups, to be stable in 6 *m* NaOH(aq) at 90 ºC; instead it was found to be degraded to oxalate (Table 4). This reactivity may be attributed to the presence of acidic hydrogen atoms (at C2 and C3) adjacent to carboxylate groups. Oxidative cleavage of the C2–C3 bond in tricarballylate looks plausible since it would yield three equivalents of oxalate, which was the only degradant detected in solution (Table 5). Further experimental work would be required to elucidate the precise mode of degradation of tricarballylate.

Both the epimeric polyalcohols D-glucitol and D-mannitol produced lactate, oxalate, acetate and formate in 6 *m* NaOH(aq) at 90 °C. The reactivity of the polyalcohols is attributed to the presence of multiple hydroxyl groups. With the exception of lactate, all these species have been reported previously as degradation products from these parent compounds under various reaction conditions (Loh et al., 2008a, 2010). A mechanism for the decomposition of the polyalcohol threitol in NaOH(aq) has been proposed by Loh et al. (2010), which can be applied to D-glucitol and D-mannitol to explain their degradation to formate and oxalate. However, further investigation will be required to account for the concomitant production of lactate and acetate.

Amongst the limited number of aliphatic species studied at 180 °C (Table 4), only propanoate was found to be stable. This stability is consistent with that observed for other non-hydroxylated aliphatic carboxylates containing less than five carbon atoms (Tardio et al., 2004b; Xiao et al., 2007; Machold et al., 2009) and implies that propanoate might be a degradation product of larger organic species. Propanoate has indeed been reported to be present in industrial Bayer liquors (Guthrie et al., 1984; Baker et al., 1995; Xiao et al., 2007) although it has not been detected in our studies.

3.2 Reactions of aromatic compounds

While the presence of hydroxyl substituents in aliphatic species, with the exception of benzilate (see above), favours reactivity in NaOH(aq), no such uniform effect was observed for hydroxylated aromatics. Thus resorcinate, 2,4-dimethylphenolate, 3-hydroxybenzoate and vanillate degraded in NaOH(aq) at 90 °C whereas phenolate and 5-hydroxyisophthalate were stable even at 180 °C (Table 4). Nor was there any obvious correlation between the hydroxyl substitution pattern and reactivity. For example, 3-hydroxybenzoate degraded in 6 *m* NaOH(aq) at 90 °C (Table 4) as did 2-hydroxybenzoate (salicylate) but 4-hydroxybenzoate was stable at this temperature (Machold et al., 2009). Similarly, neither the presence nor the position of other substituents on the various phenolates studied was related to reactivity in any obvious way (Table 4). While lower reactivity in hydroxylated aromatics must at least in part be attributable to resonance stabilisation of the deprotonated hydroxyl moiety (i.e., the phenolate anion), this does not explain the observed differences. It is noteworthy that phenolate, which was previously reported (Machold et al., 2009) as a decomposition product of phenolic carboxylates in NaOH(aq), has been confirmed here to be unreactive up to 180 °C (Table 4).

All investigated aromatic anions possessing only carboxylate substituents were found to be stable in 6 *m* NaOH(aq) at 90 °C (Table 4) regardless of whether they were single ring (furanoate, trimellitate, pyromellitate) or fused ring (1-naphthoate and 9-anthroate). Three of the five species were studied at 180 °C (Table 4) only the heterocyclic 2-furanoate was reactive. The relative stability of LMW aromatics under

Bayer process conditions has been reported by others. In particular, Lever (1978) showed that in industrial BLs the percentage of aromatic carboxylates relative to all detectable LMW organics was 55 % in a low temperature (135 °C) plant liquor but 81 % in a high temperature (240 °C) one; the corresponding values for aliphatic carboxylates were 31 and 7 %, respectively.

Identification of the degradation products of the present aromatic anions was problematic. Where decomposition occurred, HPLC analysis of the reaction mixtures decreases in the peak area of the parent compounds (Table 4). Such decreases were accompanied by the appearance of numerous small peaks attributable to degradation products. The retention times of these small degradant peaks were shorter than those of the parent compounds suggesting the former were more polar. The UV-Vis spectra recorded at these HPLC peaks indicated that the degradants contained conjugated moieties ($\lambda_{max} \approx$ 240-380 nm). Unfortunately, ^{13}C-NMR spectra of the same solutions only showed signals for the parent compounds, which reflects the poor sensitivity of this technique relative to UV-Vis spectroscopy. Since the reaction products could not be identified, no degradation pathways are proposed for the aromatic compounds studied.

4. Concluding remarks

The present results for the interaction of nineteen organic species with hot concentrated NaOH(aq) extend the breadth of our previous observations (Machold et al., 2009), by covering polyalcohols and phenolates as well as additional aliphatic and aromatic carboxylates. This work confirms that both aliphatic and aromatic

carboxylates with hydroxyl groups tend to degrade in NaOH(aq) even at 90 °C but also provides evidence that the hydroxyl substituent position can be important. Species without hydroxyl substituents tend to be stable up to 180 °C on a long time scale. Oxalate, acetate, and formate, which are known constituents of industrial Bayer liquors, are confirmed as the major degradation products of the reacting organics although lactate was also detected in some cases. The formation of oxalate and acetate from the hydroxylated aliphatic carboxylates can be explained in terms of well-known organic reaction mechanisms but further investigation is required to account for the formation of formate and lactate. Consistent with Bayer industry experience, aromatic species appear to be less reactive than aliphatics but the reaction pathways and products are yet to be identified.

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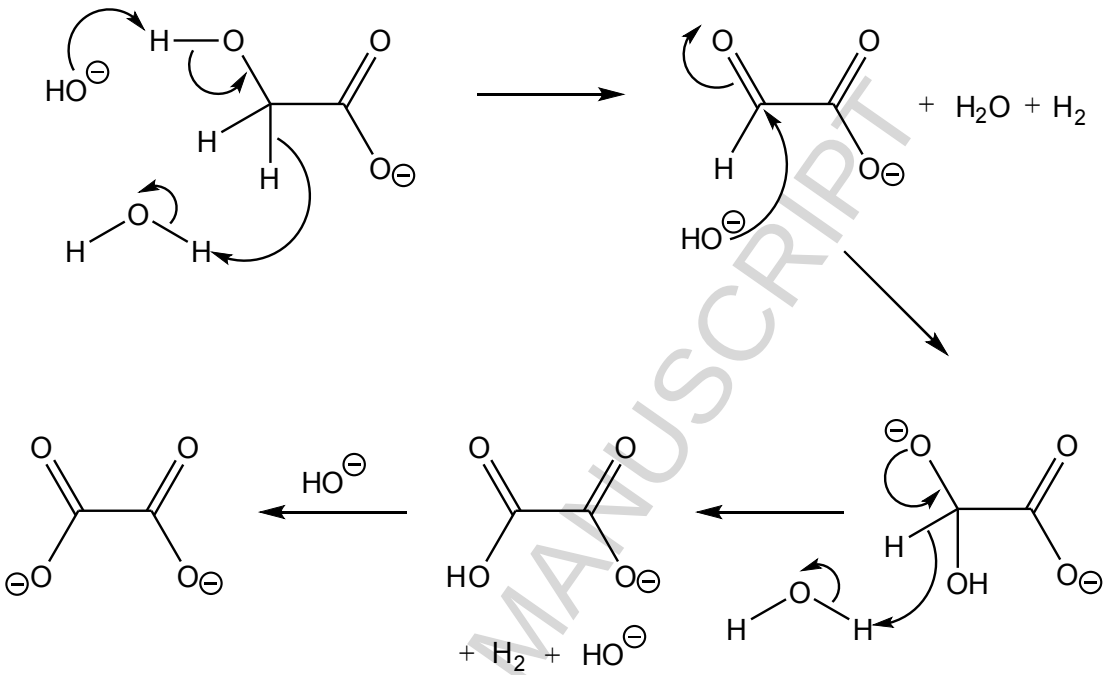


Figure 1. Ionic mechanism, including base catalysed oxidation by water (Loh et al., 2008b), proposed for the formation of oxalate from glycolate.

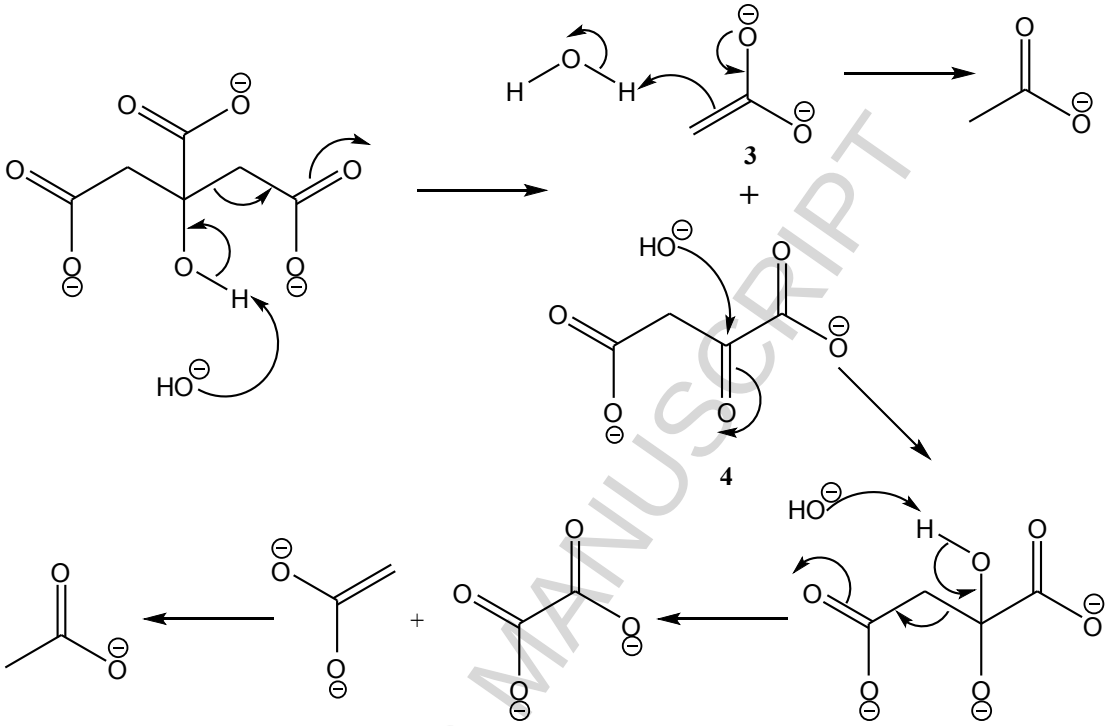


Figure 2. Proposed ionic mechanism involving retro-aldol condensation and nucleophilic acyl substitution for the formation of oxalate and acetate from citrate.

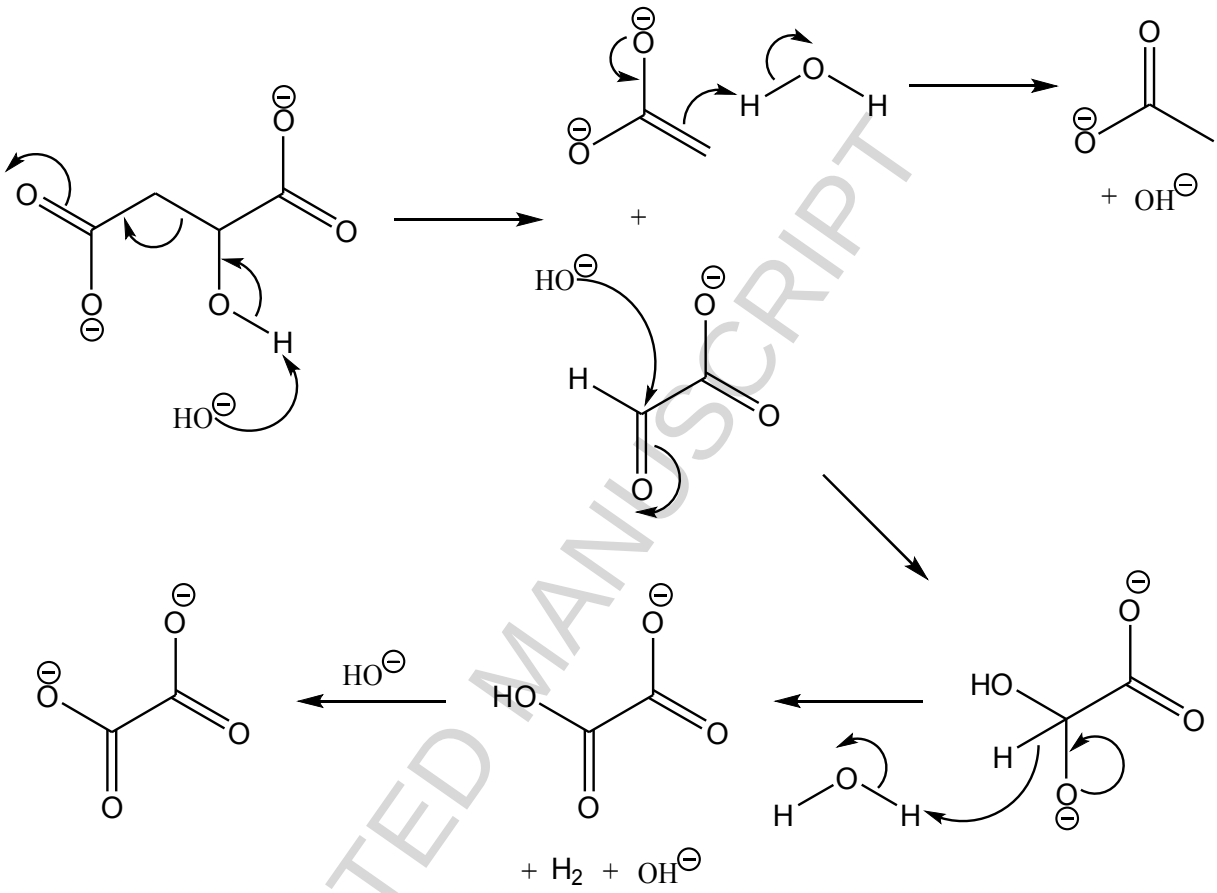


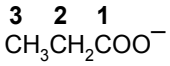
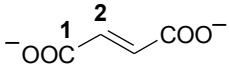
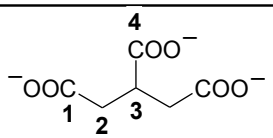
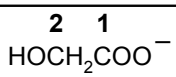
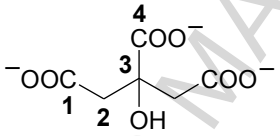
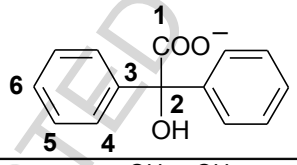
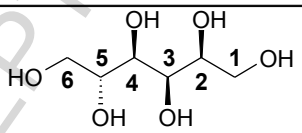
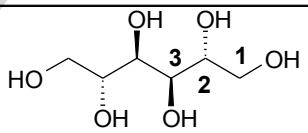
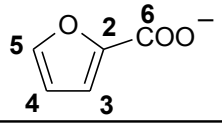
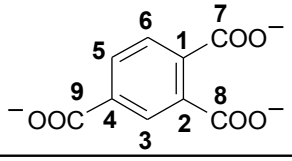
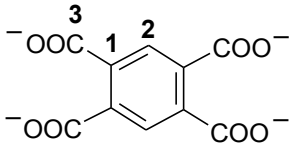
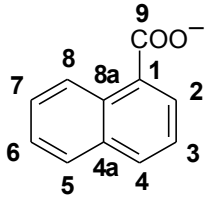
Figure 3. Ionic mechanism proposed for the formation of oxalate and acetate from malate (Machold et al., 2009).

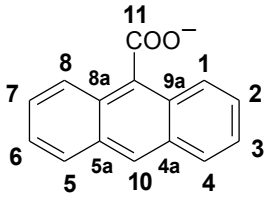
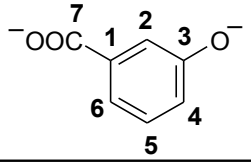
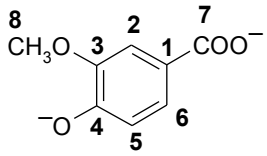
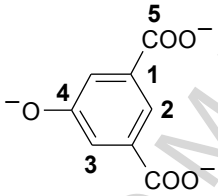
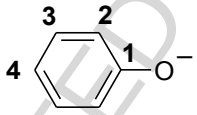
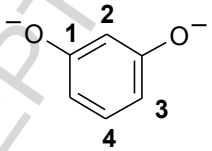
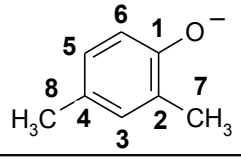
Table 1. Justifications for selection of the present organic species.

Species	References
propanoate [a]	Personal communication
fumarate [b]	Erickson et al., 1959; Machold et al., 2009
tricarballylate [a]	Guthrie et al., 1984
glycolate [a, c]	Niemelä, 1990; Guthrie et al., 1984
citrate [a]	Tardio et al., 2005
benzilate [a,c]	Guthrie et al., 1984; Niemelä, 1990
D-glucitol [d,e]	Ellis et al., 2002; Loh et al., 2008a,b
D-mannitol [d,e]	Ellis et al., 2002; Loh et al., 2008a,b; Alamdari et al., 1993
2-furanoate [d]	Ellis et al., 2002
trimellitate [a]	Guthrie et al., 1984; Lever, 1978
pyromellitate [a]	Guthrie et al., 1984; Lever, 1978
1-napthoate [f]	Wilson et al., 1999
9-anthroate [f]	Wilson et al., 1999
3-hydroxybenzoate [a,d]	Ellis et al., 2002
vanillate [d]	Ellis et al., 2002
5-hydroxyisophthalate [e,g]	Wilson et al., 1998
phenolate [g,h]	Machold et al., 2009; Wilson et al., 1999
resorcinate [d]	Ellis et al., 2002
2,4-dimethylphenol [a,f]	Wilson et al., 1999

[a] Found in BLs
[b] Product of malate decomposition in alkaline solution
[c] Product of wood decomposition in alkaline solution
[d] From degradation of plant extracts from 3 species known to occur on bauxite deposits
[e] Inhibit gibbsite precipitation or adsorb on gibbsite
[f] Model for compounds of similar structure found in BLs
[g] Product of humic acid decomposition in alkaline solution
[h] Product of hydroxybenzoate decomposition in alkaline solution

Table 2. ^{13}C-NMR chemical shifts for the present investigated organics in 6 *m* NaOD/D_2O.

Species/Compound	Structure	^{13}C-NMR Chemical Shifts δ_C (carbon number)
Aliphatic		
propanoate [a]		184.4 (**1**); 30.6 (**2**); 10.3 (**3**)
fumarate [a]		174.5 (**1**); 135.3 (**2**)
tricarballylate		184.8 (**4**); 182.3 (**1**); 44.1 (**3**); 41.4 (**2**)
glycolate		183.8 (**1**); 62.8 (**2**)
citrate		183.0 (**4**); 180.2 (**1**); 75.9 (**3**); 47.1 (**2**)
benzilate		181.1 (**1**); 145.8 (**3**); 128.9 (**4**); 128.4 (**6**); 128.1 (**5**); 84.0 (**2**)
D-glucitol		75.1 (**5**); 74.9 (**3**); 74.0 (**2**); 72.0 (**4**); 65.0 (**1**); 64.1 (**6**)
D-mannitol		74.2 (**2**); 73.8 (**3**); 65.0 (**1**)
Aromatic		
2-furanoate		167.1 (**6**); 150.1 (**5**); 145.9 (**2**); 115.6 (**4**); 112.7 (**3**)
trimellitate		178.2 (**7**); 177.6 (**9**); 175.3 (**8**); 141.2 (**1**); 137.9 (**4**); 137.0 (**2**); 130.2 (**5**); 128.6 (**3**); 127.8 (**6**)
pyromellitate		177.5 (**3**); 138.6 (**1**); 126.8 (**2**)
1-naphthoate		178.5 (**9**); 138.3 (**4a**); 133.9 (**4**); 129.9 (**8a**); 129.8 (**2**); 129.1 (**5**); 127.6 (**1**); 127.0 (**7**); 126.5 (**6**); 126.3 (**8**); 125.4 (**3**)

9-anthroate		– [b]
3-hydroxybenzoate		177.1 (**7**); 166.9 (**3**); 138.5 (**1**); 130.3 (**5**); 122.6 (**6**); 119.8 (**4**); 115.8 (**2**)
vanillate		176.8 (**7**); 162.1 (**4**); 150.7 (**3**); 125.6 (**6**); 120.8 (**1**); 118.3 (**2**); 113.9 (**5**); 56.8 (**8**)
5-hydroxyisophthalate		176.8 (**5**); 166.9 (**4**); 138.2 (**1**); 122.6 (**2**); 116.3 (**3**)
phenolate [a]		165.8 (**1**); 129.7 (**3**); 118.7 (**4**); 114.5 (**2**)
resorcinate		168.6 (**1**); 130.8 (**4**); 109.3 (**3**); 106.8 (**2**)
2,4-dimethyl-phenolate		163.0 (**1**); 131.8 (**3**); 128.1 (**4**); 127.9 (**5**); 123.8 (**4**); 118.6 (**6**); 20.5 (**8**); 17.9 (**7**)

[a] Recorded in 6 *m* NaOH(aq)
[b] No NMR data were obtained for 9-anthroate due to its low solubility in 6 *m* NaOD

Table 3. HPLC retention times (t_r) and wavelength of absorbance maxima (λ_{max}) for the acid forms of the investigated species.

Compound	t_r / min [a]	λ_{max} / nm [a]
Aliphatic		
propanoic acid	2.2	206
fumaric acid	8.1	203
tricarballylic acid	8.2	203
glycolic acid	2.3	203
citric acid	6.1	207
benzilic acid	6.4	203; 249; 258
D-glucitol [b]	–	–
D-mannitol [b]	–	–
Aromatic		
2-furanoic acid	2.5	203; 222; 244
trimellitic acid	1.9	203; 222; 244; 284
pyromellitic acid	1.5	203; 221; 244; 294
1-napthoic acid	8.8	218; 294
9-anthroic acid	14.6	221; 252; 345; 362; 381
3-hydroxybenzoic acid	2.6	203; 221; 236; 297
vanillic acid	2.5	203; 222; 245; 273
5-hydroxyisophthalic acid	2.0	203; 221; 310
phenol	4.1	203; 271
resorcinol	2.4	203; 218; 268
2,4-dimethylphenol	8.9	203; 278

[a] Determined using the HPLC UV/Vis detector of the HPLC instrument on 0.1 *m* aqueous solutions of the organic compound, acidified to pH 2.0.

[b] Could not be determined using UV/Vis detection.

Table 4. Stability of LMW organics in 6 *m* NaOH at 90 and 180 °C.

Species/Compound	**Stability** [a]			
	90 °C			180 °C
	12 d	24 d	36 d	12 d
Aliphatic				
propanoate	S	S	S	S
fumarate	D(80)	D(85)	D(88)	D [b]
tricarballylate	D(3)	D(12)	D(25)	N
glycolate	D(7)	D(10)	D(17)	N
citrate	D(12)	D(17)	D(30)	N
benzilate	S	S	S	D
D-glucitol	D	D	D	N
D-mannitol	D	D	D	N
Aromatic				
2-furanoate	S	S	S	D [b]
trimellitate	S	S	S	S
pyromellitate [c]	S	S	S	S
1-napthoate [c]	S	S	S	N
9-anthroate [c]	S	S	S	N
3-hydroxybenzoate	D(6)	D(9)	D(14)	D [b]
vanillate	D(7)	D(10)	D(15)	N
5-hydroxyisophthalate [c]	S	S	S	S
phenolate	S	S	S	S
resorcinate [d]	D(7)	D(18)	D(28)	N
2,4-dimethylphenolate [d,e]	D	D	D	N

[a] S = stable (see text), D = decomposing, N = not studied; numbers in parentheses are approximate decomposition percentages determined from HPLC peak areas.

[b] Tested for 2 d (fumarate), 3 d (2-furanoate), or 7 d (3-hydroxybenzoate).

[c] Precipitated when acidified but still detectable by HPLC.

[d] Some decomposition occurred prior to heating.

[e] No quantification possible due to unresolved HPLC peaks.

Table 5. Main solution products detected in this study for reaction mixtures of 0.1 *m* aliphatic species with 6 *m* NaOH solution at 90 °C.

Initial species/compound [a]	**Main products** [b]
fumarate	malate, oxalate, acetate
tricarballylate	oxalate
glycolate	oxalate
citrate	oxalate, acetate
D-glucitol	lactate, oxalate, acetate, formate
D-mannitol	lactate, oxalate, acetate, formate

[a] Propanoate not listed here because it was found to be stable up to 180 °C
[b] Listed in order of decreasing molar mass

Research highlights

- The behaviour of nineteen phenolates, polyalchohols and carboxylates in hot concentrated NaOH(aq) is reported and reaction products partially characterised.
- Lactate has been detected from the degradation of polyalcohols, in addition to the known products acetate, oxalate, and formate.
- Previously reported features of the reactivity of organic species in NaOH(aq) such as the stablility of unsubstituted carboxylates, the reactivity of hydroxylated species, and the relative stability of aromatic species have been confirmed. It is suggested that the reactivity of compounds is related to the position of the hydroxyl substituent and the type of leaving group present.